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MEMBRANE APPLICATIONS IN GRAPE JUICE AND WINE PROCESSING

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Gray Davis, *Governor*

Membrane Applications in Grape Juice and Wine Processing

An Interim Report based on Membrane Trials Conducted at
E. & J. Gallo Winery, Fresno, California. November 2000 – April 2001

Sponsored by the California Energy Commission, Sacramento, California

Jatal D. Mannapperuma
CIFAR, University of California, Davis

Executive Summary

Twelve membrane applications were investigated during this period with varying degrees of success. Treatment of distill material and ion exchange wastewater were placed at a higher priority due to the urgency of the disposal situation. Trial results of these applications were used to prepare specifications for full-scale membrane systems and were used to invite bids from system suppliers. More rigorous long term testing of these applications was highly desirable but could not be accomplished due to the demands of the situation.

A microfiltration system was proposed to concentrate tank bottoms during the crushing season. It will feed the permeate to the still and store the retentate. During the off-season it will reprocess the retentate by diafiltration to recover more alcohol. Several other high suspended solids plant streams like, wine bottoms, juice and juice bottoms will also be processed by the system during off-season.

The capital cost of a 200,000 gpd microfiltration system is estimated at $450,000 and the operating cost at $2.33 per kgal. These estimates are considered favorable compared to other alternatives. The same microfiltration membrane was tested with several other feed streams like, still bottoms, wine lees, sweet wine and high solids juice with satisfactory results. Reported cost of present press filtering operation is $20 per kgal. Therefore, proposed microfiltration system can be used to replace at least some of the press filtering operations with significant savings.

The plant treats juice and some wines by cation exchange. The ion exchange columns are regenerated using 5% sulfuric acid. The cost of disposal of IXWW is estimated at $30 per kgal. *Membrane trials indicated that IXWW could be concentrated two fold by reverse osmosis. A single pass membrane system to reduce IXWW volume by 50% was estimated at $130,000. The estimated operating cost of $3.73 per kgal, which compares favorably with cost of present operation.*

The present method of juice treatment is expensive, time consuming and produces high waste volume. A continuous juice treatment system using ultrafiltration followed by granular activated carbon (GAC) absorption columns is proposed as an alternative. This on-line process is less costly and produces less waste. More rigorous testing is required to design this process.

Wine stabilization and clarification using membrane is an alternative to cold stabilization. This membrane application will be investigated during the crushing season when unstable wine is available. Electrodialysis (ED) is another alternative for cold stabilization. The reported operating cost and energy consumption for electrodialysis are substantially less than for cold stabilization. A demonstration of electrodialysis is also planned during the crushing season.

The plant uses potassium hydroxide (KOH) for cleaning evaporators and stills and tartaric acid (TA) in wine making. Potassium bitartrate is a byproduct that can be splitted with water to produce potassium hydroxide and tartaric acid. This alternative has many advantages over the conventional tartaric acid process. A research and development effort in this direction is highly recommended.

Byproducts of distillation, aldehydes and fusel alcohols are some times mixed with still bottoms and disposed by land application. These byproducts have a fuel value of billion Btu per day and a fuel replacement value close to million dollars per year. The possibility of its use as boiler fuel and marketing as industrial alcohol should be investigated.

Membrane technology offers many opportunities for process improvement in Fresno winery. Large scale of operation makes most of these opportunities economically attractive. Some of these operations may be attractive at other wineries owned by the company. Cost and benefit estimates mentioned in this report are based on conversations with the plant management. The estimates should be verified with documented information. The information and suggestions provided by this study should be followed-up with in-depth investigations.

1.0 Background

E. & J. Gallo Winery in Fresno, California produces grape juice and wine using grapes. The plant receives about 16,000 tons of grapes per day and produces about 3.2 million gallons of juice per day during the crushing period that lasts from August to October. This juice is used to produce grape juice concentrate and for fermentation into wines.

Wine is used for retail or distilled to produce brandy. Juice concentrate is reprocessed into several products. All the sugar rich residues, such as, juice treatment tank bottoms are fermented and mixed with fermentation residues rich in alcohol and distilled to produce food grade alcohol.

The reject stream from the still after removal of alcohol is high in suspended and dissolved organic matter. The current practice is to dispose the still bottoms by land application. Suspended solids in the still bottoms accumulate on the land and create a barrier for percolation of liquid. This creates liquid pools that give rise to odor and infestation problems. Removal of suspended matter from still bottoms is expected to alleviate this situation. The suspended matter concentrated by membrane treatment can be disposed by composting. Microfiltration can achieve this objective.

Processing of juice and stabilization of wine involves cation exchange to replace potassium by hydrogen ions. The ion exchange columns are regenerated using 5% sulfuric acid. *Spent acid and rinse water are collectively called ion exchange waste water (IXWW). Disposal of IXWW is an expensive operation. Membrane treatment can reduce the IXWW volume and also recover some acid for reuse.*

Reprocessing of grape juice concentrate involves treatment by gelatin, bentonite, activated carbon, and silica for removal of tannins, proteins, color and other impurities and filtering using DE. Membrane treatment has the potential for replacing most of these expensive treatment steps

Wine and juice processing involves several other opportunities for membrane filtration. Juice clarification, wine clarification, wine stabilization, recovery of wine and juice from tank bottoms, sterilization of wines are some of these. The objective of membrane trials conducted at Fresno Winery was to test and demonstrate these membrane applications.

2.0 Membrane Treatment Trial Summary

The membrane test and demonstration unit was stationed at the winery for about 12 weeks. Sixty Seven membrane trials were conducted with twelve different feed sources during this period. The objectives of these trials are summarized in Table 1

Table 1. Membrane Trial Summary

	Source	Objective	Membrane Treatment
1	Distil Matter (DM)	Clarification	Microfiltration
2	Wine Lees	Clarification	Microfiltration
3	Sweet Wine	Sterilization	Microfiltration
4	Treatment Bottoms	Clarification	Microfiltration
5	High Solids Juice	Clarification	Microfiltration
6	Still Bottoms	Clarification	Microfiltration
7	Still Bottoms Microfiltrate	BOD reduction	Reverse Osmosis
8	Juice Concentrate	Decolorization	Ultrafiltration
9	Wine	Stabilization	Nanofiltration
10	Ion Exchange Waste Water (IXWW)	Concentration	Reverse Osmosis
11	Ion Exchange Waste Water (IXWW)	Acid Recovery	Nanofiltration

3.0 Clarification of Distill Material (DM)

The plant has three stills that are identified by their diameter expressed in inches as 96, 84 and 72. The rated capacities of these stills are 15,000 gallons, 8,000 gallons and 7200 gallons of feed per hour respectively. Wine tank bottoms, treatment bottoms and other fermentation byproducts collectively called distill material (DM) are distilled in the 96 still to produce food grade neutral spirits (NSFG). Wine fermented for brandy making; called Gallo brandy designate (GBD) is distilled in 84 and 72 stills.

Microfiltration of distill material has the advantage of cleaner and easier operation of the still. Still bottoms will be virtually free of suspended solids that hinder land application. Primary disadvantage of microfiltration of still feed is the need for diafiltration to reduce the alcohol content. This will require additional membrane area. Also it increases the hydraulic load on the still. Other disadvantage is that still feed has to microfiltered at about 165 F to prevent boiling of alcohol compared to still bottoms, which can be microfiltered at about 190F. This results is substantial lowering of permeate flux and increasing the membrane area. The plant management feels that the advantages of treating still feed outweigh its disadvantages. Therefore, microfiltration of still feed was studied in more detail during the project.

Selection of microfiltration membrane for this application is limited to tubular systems due to high suspended solid content of still feed. Graver microfiltration membrane rated at 0.1 μm is well suited for this application. This membrane consists of 3/4-inch diameter sintered stainless steel tubes with a titanium oxide filtration layer. It does not have temperature limitation like polymeric membranes. Wide diameter and high temperature capability makes this membrane ideally suited for stillage application. The possibility of Membralox ceramic membranes was eliminated due to smaller (6 mm) tube diameter and high cost (about 2 to 3 fold). Tubular polymeric membranes were ruled out due to inferior high temperature capability and poorer chemical resistance.

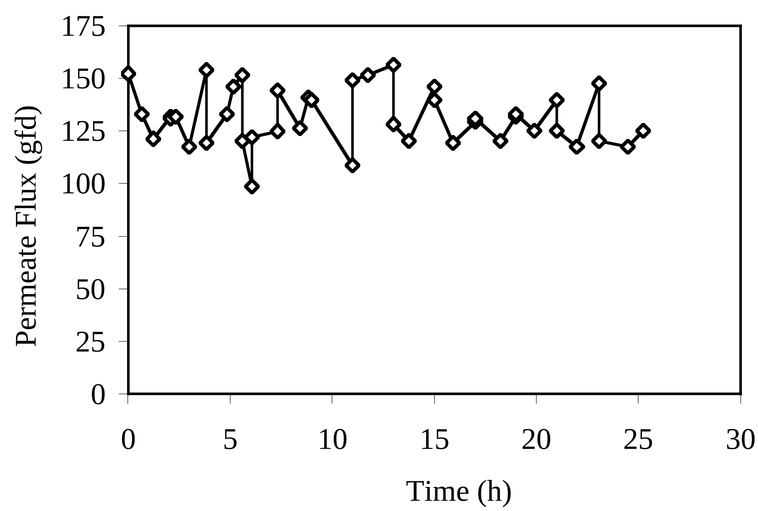
3.1 Microfiltration of DM

Several microfiltration trials were conducted with still feed using the Graver microfiltration membrane. These included concentration scans, pressure scans, and velocity scans. The results of these scans were used to select the optimum operating points for the design of the system. Finally a time scan was conduced over a two-day period to observe the long-term performance of the system under selected operating condition. These operating conditions were

Temperature	165 F
Trans membrane pressure	48 to 52 psi
Recirculation flow rate	75 to 80 gpm
Module pressure drop	2-3 psi
Suspended solids content	10 to 58%

The trial was designed to simulate feed and bleed operation. DM at about 20% volumetric suspended solids was selected as feed for these trials. The feed tank was filled with feed, heated to 165F by recirculation through the heat exchanger. The feed volume was concentrated twofold by draining the permeate. This procedure was repeated thirteen times over a two-day trial. Permeate fluxes observed in this trial are shown in Figure 1

Figure 1. Flux Characteristics During Microfiltration of Heavy Stillage



Permeate fluxes were quite stable this long-term trial. The membrane was in operation for over 40 hours during the trial including startup, feeding and heating intervals. The membrane was not cleaned during this period. Volumetric suspended solids content varied from a low of 10% to a high of 58%. The performance observed during this trial is quite encouraging. The trial nearly encompassed the expected operating suspended solids range from 12% to 60% and the expected continuous operating period of 21 hours.

3.2 Module Hydraulics

Electrical energy to drive the recirculation pumps is expected to constitute about 75% of the operating cost of the microfiltration system. Therefore, selection of recirculation pumps is critical for the economics of system operation. The process fluid has to be characterized under actual operating conditions to gather data for use in pump sizing.

The industrial Graver module will use 3/4 inch diameter 20ft long tubes. Therefore, a similar pipe was used to obtain pressure drop vs. flow rate characteristics for DM at several solids contents. Another set of hydraulic characteristics was obtained for the Graver test module, which consists of four 3/4 inch diameter, 5 ft long tubes as a confirmatory measure. This set was also obtained at several solid contents of process fluid.

Hydraulic characteristics obtained for the 20ft tube and the graver module agree well with each other. The pressure drop recorded by the process fluid is very similar to water in spite of very high suspended solids and very thick consistency. The manufacturer suggests operating the module at a flow rate of about 20 gpm per tube. At this flow rate the pressure drop varies from about 2 psi at 20 %v/v to 3.5 psi at 60% v/v suspended solids for a 5 ft long tube. These values were used to specify following the hydraulic characteristics for the module.

Higher flow rates produce higher permeate fluxes and result in smaller membrane area. However, electrical power requirement increases with the third power of the flow rate. Therefore, it is not considered economical to use higher flow rates.

3.3 Economics Assessment

A preliminary economic assessment of a membrane system to produce 200,000 gallons of permeate per day was prepared based on trials results for budgetary comparison with alternative technologies. A system comprising of three identical stages with 20% allowance for cleaning was considered in the evaluation. Total membrane area was estimated at 3,000 sft based on an assumed 80 gfd average flux. Each stage contains one membrane module with 1,000 sft of membrane area and a 75 hp recirculation pump rated at 2,700 gpm at 30 psi. The feed pump for the system is rated at 200 gpm at 30 psi and driven by a 5 hp motor.

The capital cost of the membrane system is estimated at $450,000 based on an average cost of $150 per sft of membrane area. Major operating cost is the electric power used to drive the pumps. Cleaning chemicals and operating labor are the other operating costs. Cleaning is done using a 2% caustic solution on a daily basis. Caustic requirement is about 100 lb per day. The preliminary economic assessment based on these assumptions is summarized in Table 2.

Table 2. Economic Assessment of Microfiltration System

System Parameters	
Microfiltration membrane area (sft)	*3,000*
Capital investment ($)	*450,000*
Electric power (kW)	*160*
Hours of operation (hours/day)	*24*
Days of operation (days/year)	*150*
Permeate production (Mgal/year)	*30*
Expenses ($/year)	
Energy cost (576MWh @ $80)	*46,100*
Cleaning caustic (15,000lb @ $0.4)	*6000*
Labor (6 hours per day @ $20)	*18,000*
Total operating costs	***70,100***

The total operating cost amounts to about $2.33 per kgal. This estimate should be compared with estimated costs of other alternative technologies. Electricity for pumps amounts to about 66% of the total operating cost. Therefore, this estimate is extremely sensitive to future changes in electricity cost. Infrastructural needs like buildings, electricity lines and substations, feed and return pipelines, steam lines, reject collection and disposal systems have to be provided to complete the membrane system. The cost of these items should be included in the economic assessment to improve its accuracy.

4.0 Clarification of Wine Lees and Sweet Wine

Conventional process of raking of wines leaves about 13% of the volume as lees at the bottom of the tank. This fraction ends up as DM and used for production of NSFG. Microfiltration can recover a substantial portion of this volume as wine that has a higher value. Microfiltration system designed for DM can be used for this application during the off-season.

One membrane trial was conducted with Graver microfiltration membrane at 50 psi pressure and 140 F temperature to evaluate this application. Heavy forming was a problem during this trial.

The permeate fluxes observed in this trial is shown in Figure 2. About 70% of the lees volume was recovered as clear permeate during the trial. Permeate fluxes were relatively stable.

Rejection characteristics observed during the trial are summarized in Table 3. Final retentate contained 30.7% suspended solids on gravimetric basis and 75% suspended solids on volumetric basis. The final product of the trial was a very thick paste when cooled to ambient temperature. The permeate samples developed substantial quantities of white crystals upon cooling. This was not observed in feed or retentate samples.

Figure 2. Flux Characteristics During Microfiltration of Wine Lees

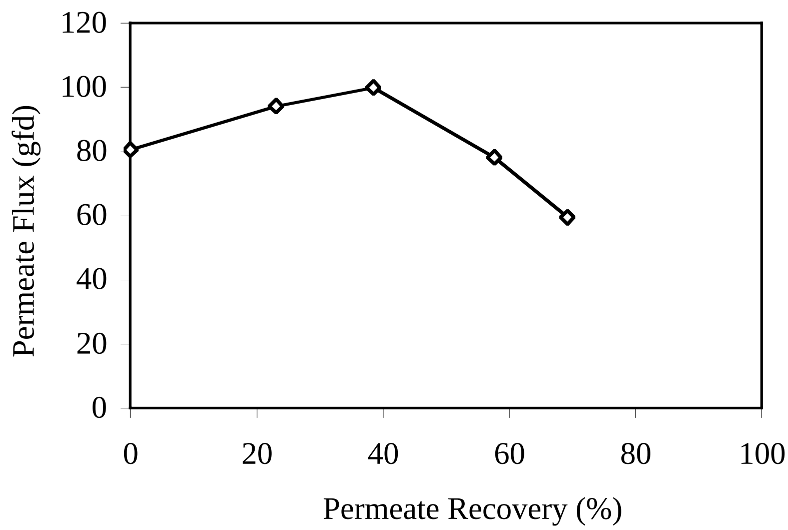


Table 3. Rejection Characteristics during Microfiltration of Wine Lees

Recovery (%)	EC (μS/cm)		Total Solids (mg/L)		Suspended Solids In Retentate	
	Retn.	Perm.	Retn.	Perm.	(% w/w).	(% v/v).
0	8,660	8,270	128,600	45,600	8.3	16
38	6,900	8,910	183,200	54,200	12.9	30
69	6,240	12,760	365,000	58,300	30.7	75

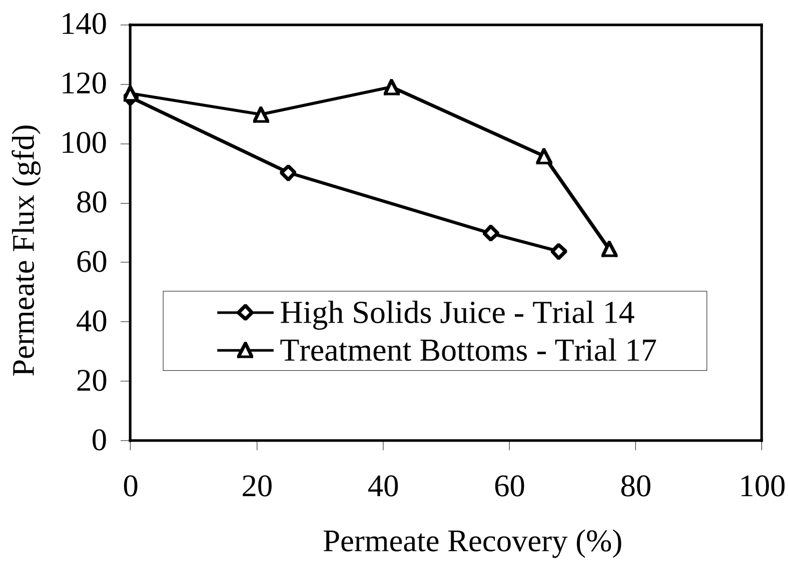
Production of sweet wine requires the fermentation to be stopped before all the sugar in the medium is converted to alcohol. At present this is done by removing the yeast through centrifugation. Microfiltration is a better alternative method of removing yeasts from the medium.

A short microfiltration trial of 30-minute duration was conducted using Graver microfiltration membrane rated at 0.1 μm to demonstrate this alternative approach. The trail was conducted at 68 F temperature and 50 psi pressure. Permeate flux observed was about 60 gfd. The feed wine recorded 9 brix. The permeate sample was tested and found to be free of yeasts as expected.

5.0 Clarification of High Solids Juice and Treatment Bottoms

Microfiltration of high solids juice would clarify it prior to evaporation. Microfiltration of treatment bottoms could recover additional juice. Graver microfiltration membrane rated at 0.1 μm was used in the trials with these two sources. Permeate fluxes observed in these trials are shown in Figure 3. Treatment bottoms produced higher fluxes than high Solids juice in spite of its higher suspended solids level.

Figure 3. Flux Characteristics During Microfiltration of High Solids Juice and Treatment Bottoms - Graver Tubular Membrane Pressure 50 psi – Temperature 140 F



Rejection characteristics observed during the high solids Juice trial are summarized in Table 4. The trial recovered 68% of the feed as permeate. Final retentate contained 28% suspended solids on volumetric basis. However the suspended solids on gravimetric basis was negligibly small. The reason for this behavior is not clear.

Rejection characteristics observed during the Treatment bottoms trial are summarized in Table 5. This trial recovered 76% of the feed as permeate. Final retentate contained 30.2% suspended solids on gravimetric basis and 83% suspended solids on volumetric basis. The final retentate of this trial was a very thick paste when cooled to ambient temperature. Permeate produced during the trial seemed suitable for incorporation into juice but was not tested for quality.

Table 4. Rejection Characteristics during Microfiltration of High Solids Juice

Recovery (%)	EC (μS/cm)		Total Solids (mg/L)		Suspended Solids in Retentate	
	Retn.	Perm.	Retn.	Perm.	(% w/w).	(% v/v).
0	4,520	4,780	25,750	23,000	0.3	10
25	4,720	4,860	27,100	26,700	0.0	11
57	4,810	4,880	27,100	26,100	0.1	19
68	5,020	5,000	27,730	26,120	0.2	28

Table 5. Rejection Characteristics during Microfiltration of Treatment Bottoms

Recovery (%)	EC (μS/cm)		Total Solids (mg/L)		Suspended Solids in Retentate	
	Retn.	Perm.	Retn.	Perm.	(% w/w).	(% v/v).
0	n.d.	1,501	306,100	28,740	27.7	25
41	n.d.	1,592	311,900	29,030	28.3	45
76	n.d.	1,602	330,900	29,150	30.2	83

6.0 Membrane Treatment of Still Bottoms (Slop)

Microfiltration of still bottoms was the original approach to reducing the suspended solids level in land application. This approach was discontinued in favor of microfiltration of still feed in case of NSFG still. However, still bottoms from GBD operation may require clarification. Therefore a long term microfiltration trial was conducted with still bottoms using Graver membrane to evaluate this application. Operating conditions during this trial were;

Temperature	180 F
Trans membrane pressure	47 to 53 psi
Recirculation flow rate	~100 gpm
Module pressure drop	~6 psi

The trial was designed to simulate feed and bleed operation. The feed tank was filled with feed, heated to 180F by recirculation through the heat exchanger. The feed volume was concentrated four-fold by draining the permeate. This procedure was repeated several times over a three-day trial period. Permeate fluxes observed in this trial are shown in Figure 4 and quality characteristics are summarized in Table 6.

Permeate flux declined rapidly at the beginning of the trial but remained quite stable after the initial decline. The membrane was not cleaned during this period. The suspended solids content was very low during this trial similar to still bottoms from GBD operation. Therefore, this performance could be a fair representation of microfiltration of GBD still bottoms.

Figure 4. Flux Characteristics During Microfiltration of Still Bottoms

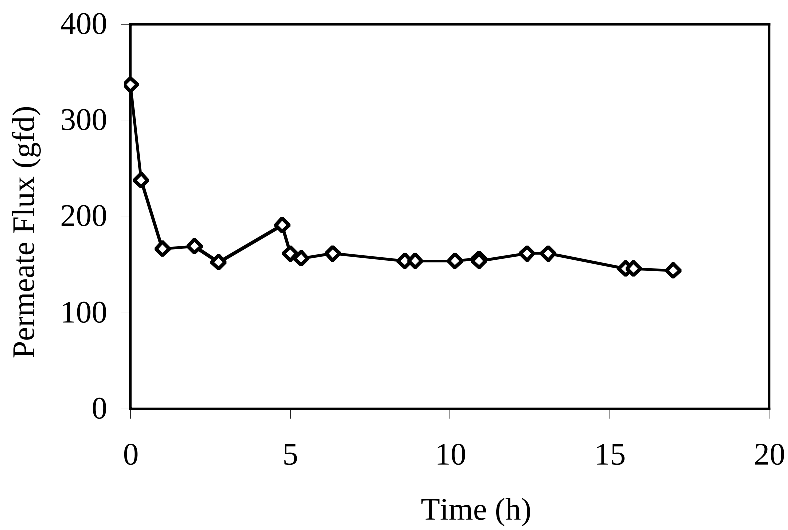


Table 6. Quality Characteristics during Microfiltration of Still Bottoms

Batch	Time (h)	Permeate Flux (gfd)	Suspended Solids (% v/v)	Suspended Solids (% w/w)	Total Solids (%w/w) Retentate	Total Solids (%w/w) Permeate
1	0.0	337.5				
	1.0	166.6	0.1	0.30	1.32	1.02
	2.8	152.7	0.2	0.27	1.01	0.74
2	4.8	191.2				
	6.3	161.6				
3	6.3	161.6				
	8.6	153.9				
4	8.9	153.9				
	10.9	156.3	0.5	0.27	1.01	0.74
5	10.9	153.9				
	12.4	161.6	0.6	0.69	1.56	0.87
6	13.1	161.6				
	15.5	146.2	0.6	0.57	2.02	1.45
	17.0	144.0				

Removal of suspended solids by microfiltration is expected to comply with environmental regulations in the dear term. However, in the long term reduction of dissolved organic and inorganic matter may become necessary. Further membrane treatment is one method of achieving this objective.

Microfiltrate from Graver trials was treated by reverse osmosis and nanofiltration to evaluate the possibility of separation of dissolved solids. Trials were conducted at high temperature (160F) and low temperature (110F) to compare the performance. Spiral membrane modules were used in all the trials since the feed is preclarified by microfiltration.

A Filmtec NF45 membrane rated at 45% NaCl rejection were used in nanofiltration trial. A PTI AFTRO and Desal SF membranes rated at 99% NaCl rejection were used in reverse osmosis trials. Figure 5 illustrates fluxes observed in these trials. The permeate flux declined rapidly with recovery. High osmotic pressure is seen as the primary reason for low fluxes. Fouling also contributes to this behavior.

The rejection characteristics are summarized in Table 7. Reverse osmosis membranes rejected over 95% of the COD under all conditions. PTI membrane produced higher rejection of COD and lower rejection of EC at 160F compared to 110F. The reason for this unusual behavior is not clear but should be investigated since it may provide important and useful information.

Figure 5. Flux Characteristics during Reverse Osmosis and Nanofiltration of Still Bottoms Pressure 450 psi

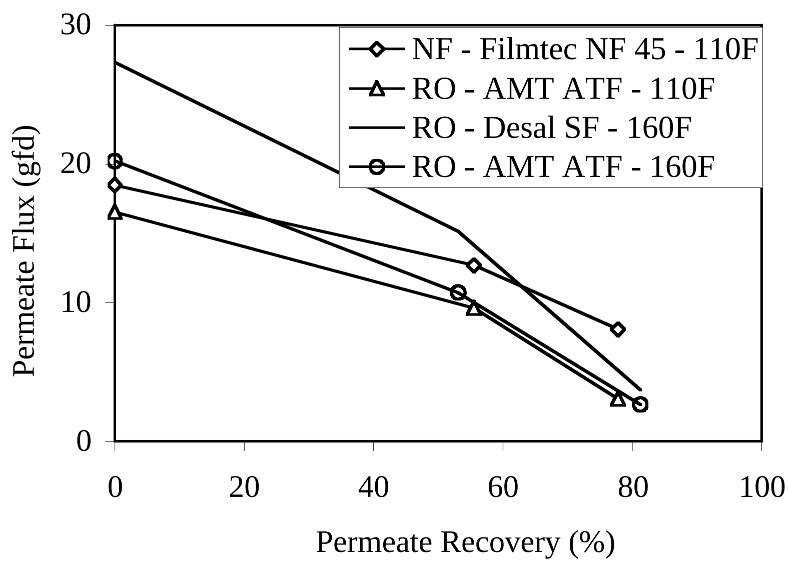


Table 7. Rejection Characteristics during Reverse Osmosis and Nanofiltration of Still Bottoms

Permeate	EC (mS/cm)		EC Rejection	COD (mg/L)		COD Rejection
Recovery (%)	Retentate	Permeate	(%)	Retentate	Permeate	(%)
Nanofiltration – Filmtec NF 45 – 450 psi – 110F						
0.0	6,260	2,650	57.7	39,750	14,400	63.8
55.6	9,630	3,810	60.4	69,600	22,600	67.5
77.8	13,480	6,120	54.6	117,300	41,650	64.5
Reverse Osmosis – PTI ATF – 450 psi – 110F						
0.0	6,260	316	95.0	39,750	1,190	97.0
55.6	9,630	438	95.5	69,600	2,050	97.1
77.8	13,480	945	93.0	117,300	5,220	95.5
Reverse Osmosis – Desal SF – 450 psi – 160F						
0.0	7,290	1,617	77.8	44,400	351	99.2
53.1	11,190	1,994	82.2	61,700	783	98.7
81.3	16,540	3,720	77.5	122,400	1,446	98.8
Reverse Osmosis – PTI ATF – 450 psi – 160F						
0.0	7,290	691	90.5	44,400	256	99.4
53.1	11,190	1,524	86.4	61,700	737	98.8
81.3	16,540	3,020	81.7	122,400	1,469	98.8

7.0 Membrane Treatment of Grape Juice Concentrate

Grape juice is concentrated to 68 brix during the crush for storage. Juice concentrate is diluted, and treated by ion exchange. It is then treated by gelatin, bentonite, activated carbon, and silica for removal of tannins, proteins, color and other impurities. Finally the treated juice is filtered using DE and reconcentrated. Membrane treatment has the potential for replacing most of these treatment steps

Removal of color is the most critical requirement. The acceptable color value is 0.05 absorbance at 430 nm. Loose nanofiltration or tight ultrafiltration can remove color bodies in the juice. Several short membrane trials were conducted to evaluate the technical feasibility of this possibility. Juice concentrate diluted to 25 Brix was used in these trials. Results of some of these trials are summarized in Table 8.

Jatal D. Mannapperuma
CIFAR, University of California, Davis

Table 8. Decolorization of Juice by Ultrafiltration

Trial	Membrane	Specifications (mwco)	Pressure (psi)	Flux (gfd)	Color value Retentate	Color value Permeate
15	PTI AF10	10,000	60	34	0.124	0.104
16	Koch HFK131	10,000	60	20	0.124	0.089
60	Koch HFK328	5,000	100	10	0.180	0.039
61	Synder XT2B	2,000	100	6	0.180	0.025

The results of these trials indicated that tight ultrafiltration was successful in removing most of the color bodies. The ultrafiltrate also satisfied other tests for haze formation. Permeate form these trials when treated by small concentrations of activated carbon reduced the color to the required level. These preliminary results were quite encouraging. Therefore, a concentration scan with diafiltration was conducted using Koch HFK328 membrane. Figure 6 illustrates permeate flux observed during this trial.

The permeate samples obtained during this trial had color values slightly above the required 0.05 level. Therefore, these samples were treated by activated carbon at 1lb/kgal and 2 lb/kgal concentrations. Table 9 is a summary of rejection characteristics and results of carbon treatment.

Figure 6. Flux Characteristics during Ultrafiltration and Diafiltration of Juice Concentrate

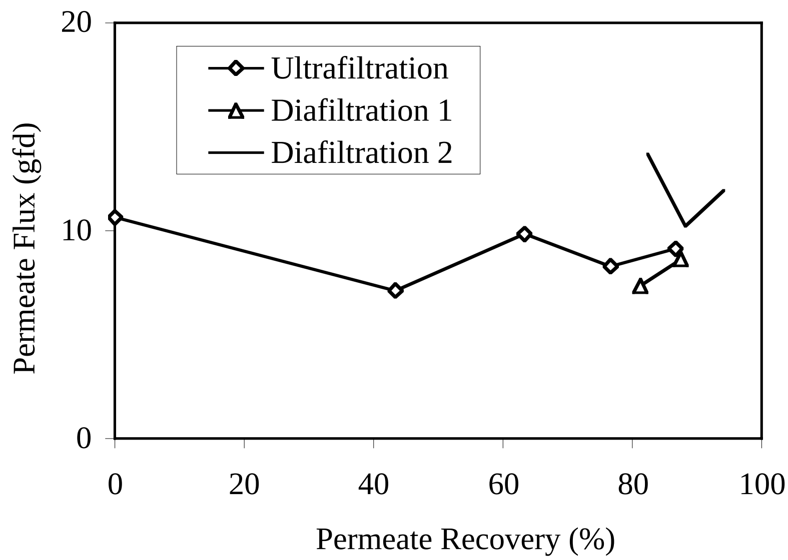


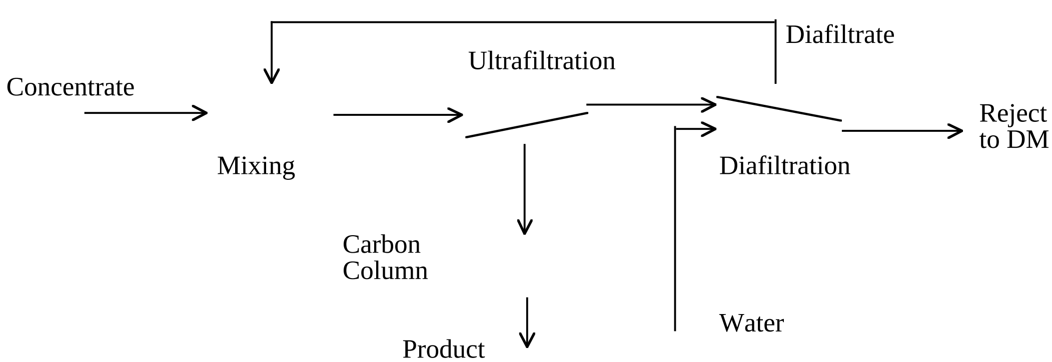
Table 9. Rejection Characteristics and Carbon Treatment of Permeate

Recovery	Brix		Color Value		Carbon Treated Permeate Color	
(%)	Retentate	Permeate	Retentate	Permeate	1 lb/kgal	2 lb/kgal
0	25.6	23.2	0.167	0.053	0.038	0.032
43.3	26.2	24.4	0.188	0.053	0.047	0.037
76.7	30.0	24.0	0.309	0.078	0.040	0.040
85.0	37.6	27.0	0.537	0.077	0.052	0.049
87.5	24.2	15.8	0.903	0.080	0.090	0.049
94.2	18.2	10.2	1.031	0.052	0.028	0.030

The results indicate that the treatment by 1 lb/kgal of carbon reduced the color value to the required level. The feed used in the trial required 8 lb/kgal of carbon to achieve the same color value. The results also indicate that ultrafiltration membrane concentrates color on the retentate side and also that diafiltration leaches sugars in preference to color. All these observations are favorable and indicate the technical feasibility of ultrafiltration as an alternative method of juice treatment.

The present treatment of juice is expensive as well as time consuming. Processing of a 550,000 gallon batch involves addition of carbon, circulating for 8 hours, addition of gelatin, bentonite and silica, circulating 3 hours, settling for 48 hours, addition of DE and press filtration. It is possible to develop continuous juice treatment system using ultrafiltration followed by carbon absorption columns. The cost of this alternative would be less than the 50% of the present treatment cost. In addition it will reduce the volume of treatment bottoms and filtration loses. A continuous juice treatment system using this concept is illustrated in Figure 7.

Figure 7. A Continuous Juice Treatment System



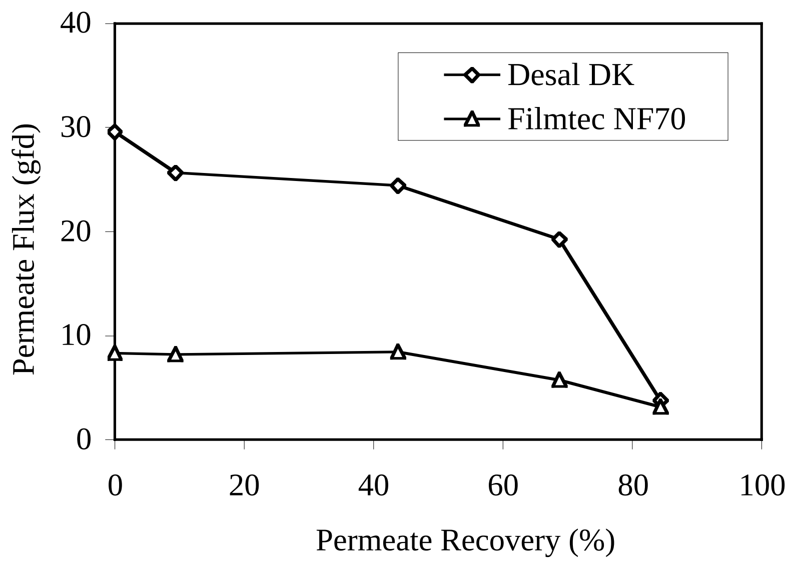
It is important to optimize this process to minimize the capital and productions costs. Tighter ultrafiltration would increase the cost of ultrafiltration but decrease or eliminate the carbon treatment cost. More membrane trial data and carbon treatment data are required to decide on the optimum configuration. The ultrafiltration trials produced highly variable but always low permeate fluxes. Improving the fluxes would reduce the capital cost drastically.

8.0 Stabilization of Wine by Membrane Treatment

Concentration of wines accelerates the KHT precipitation process substantially. Potassium bitartrate ($KHC_4H_4O_6$) has a molecular weight of 188. Therefore, it can be concentrated using a reverse osmosis or nanofiltration membranes. The optimum membrane for this application should allow significant leakage of alcohol (molecular weight 46) to minimize osmotic pressure difference across the membrane

A fractionation trial with cabernet wine was conducted using a Desal DK and Filmtec NF70 nanofiltration membranes to evaluate the feasibility of this concept. The permeate flux observed during these trials are presented in Figure 8. Permeate flux observed during these trials can be considered satisfactory under the conditions used. Higher fluxes could be obtained at higher temperatures.

Figure 8. Flux Characteristics During Nanofiltration of Cabernet Wine
Pressure 900 psi – Temperature 68 F



Tartrate crystals were observed in samples of retentate obtained at recovery levels above 40%. Several samples of retentate and permeates were analyzed for quality characteristics. The results of this analysis are summarized in Table 10.

Microfiltration of the retentate could remove the tartrate crystals. Mixing microfiltered retentate with cumulative permeate in the 16:84 ratio would produce a reconstituted wine that is stable and clarified. This was not pursued since the original wine was found to be stable after being in storage for a sufficient length of time.

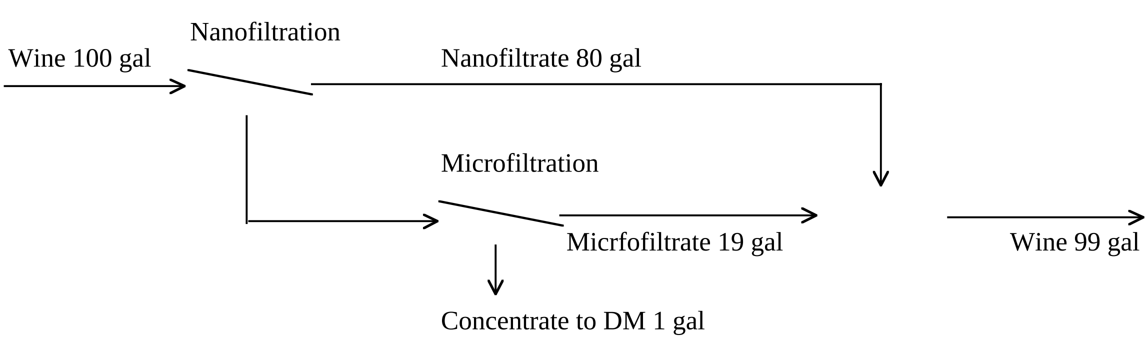
Table 10. Quality Characteristics of Wine and Fractions

	Alcohol (%)	Tartrate (mg/L)	Acidity (%)	pH
Wine	13.4	2,595	0.57	3.57
Retentate	14.8	6,200	2.48	3.49
Permeate DK (at 84% recovery)	15.3	958	0.43	3.79
Permeate NF70 (at 84% recovery)	13.7	133	0.06	4.22
Permeate Mixed Cumulative	13.4	555	0.21	3.79

Cold stabilization of wine involves storage at 26F for about 20 days. A previous study found that the cost of refrigeration is about $10.25 per kgal while the cost of chilled storage is about $10.80 per month per kgal. Based on these data the cost of cold stabilization is about $17.45 per kgal. It is possible to develop a membrane system to continuously stabilize and clarify wine on-line at a lower cost. Figure 9 illustrates this concept.

A major advantages in this concept is that only a fraction of the wine has to go through microfiltration and that the final product is stabilized as well as clarified. Quality of the final product is the deciding criterion.

Figure 9. Continuous Wine Stabilization and Clarification



Jatal D. Mannapperuma
CIFAR, University of California, Davis

9.0 Ion Exchange Waste Water Treatment

The plant uses cation exchange to replace potassium ions by hydrogen ions. The ion exchange columns are regenerated using 5% sulfuric acid. Spent acid and rinse water are collectively called ion exchange waste water (IXWW). The cost of disposal of IXWW, which primarily the cost of transport, is about $30 per kgal. Membrane treatment and other alternatives for reduction or elimination of this waste are of interest to the plant management.

An experiment was conducted to investigate the feasibility of neutralization of IXWW with calcium carbonate and calcium hydroxide. A sample of IXWW with pH of 1.26 and EC of 59.1 mS/cm. was used in this experiment. A 200 mL sample of IXWW was mixed with known mass of the reagent, mixed for about 1 minute and allowed to react for about one hour. The pH and EC of the sample was recorded at the end of this period.

Results of this experiment indicated that a given pH or EC was achieved with a lower mass of calcium hydroxide than calcium carbonate. The difference was 25 to 30% around the critical pH range of 5 to 6. Stoichiometrically, 75 grams of calcium hydroxide is equivalent to 100 grams of calcium carbonate in neutralization capacity. This is confirmed by the experimental results.

The lowest EC achievable by neutralization depends strongly on the amount of potassium present in the feed. The reagent requirement depends strongly on starting pH of IXWW. Neutralization of IXWW from the starting pH of 1.26 would require 11.5 g/L of calcium hydroxide. When the starting pH is 0.76 the requirement increases to 36.4 g/L. At an assumed rate of 20 g/l of calcium hydroxide per liter, neutralization requires 160 lb/kgal and costs $16/kgal at a price of $0.10 per lb. This is an expensive alternative that creates an additional waste product for disposal.

Ion exchange wash water contains unused sulfuric acid mixed with potassium sulfate released during regeneration. Concentration of IXWW by reverse osmosis will concentrate both acid and the salts. Reverse osmosis permeate can be used as rinse water and for used for diluting the concentrated acid. Nanofiltration of the RO retentate can produce a dilute acid with some salts that can be used to partially regenerate the resin.

Several reverse osmosis and nanofiltration trials were conducted with IXWW to evaluate the feasibility of this approach. PTI ATF reverse osmosis membrane and Filmtec NF45 nanofiltration membrane module was used these trials. These trials were conducted as concentration scans in pairs. Pressure was increase to maintain a steady flux until 60 bar but not higher. The samples taken during the trials were analyzed for pH, electrical conductivity (EC), Na, Ca, K, and Acidity. Separation characteristics observed during one set of trials are listed in Tables 11 and 12

Jatal D. Mannapperuma
CIFAR, University of California, Davis

Table 11. Rejection Characteristics during Reverse Osmosis of IXWW – Trial 31

Recovery	Electrical Conductivity (μS/cm)			pH			Acidity (Eq/L)		
(%)	Retentate	Permeate	% Rej	Retentate	Permeate	% Rej	Retentate	Permeate	% Rej
0.0	65,200	2,220	96.6	0.97	2.2	n.a.	0.33	0.012	96.4
48.4	105,700	2,370	97.8	0.72	2.22	n.a.	0.66	0.007	98.9
71.0	150,300	3,520	97.7	0.49	2.05	n.a.	1.05	0.011	99.0
82.3	177,100	10,100	94.3	0.35	1.63	n.a.	1.33	0.035	97.4
Recovery	Potassium (mg/L)			Calcium (mg/L)			Sodium (mg/L)		
(%)	Retentate	Permeate	% Rej	Retentate	Permeate	% Rej	Retentate	Permeate	% Rej
0.0	2,020	42	97.9	335	<5	~100	455	12	97.4
48.4	3,950	15	99.6	660	5	~100	606	9	98.5
71.0	7,040	10	99.9	510	<5	~100	1642	9	99.5
82.3	10,850	23	99.8	530	<5	~100	1901	12	99.4

Table 12. Rejection Characteristics during Nanofiltration of IXWW – Trial 30

Recovery	Electrical Conductivity (μS/cm)			pH			Acidity (Eq/L)		
(%)	Retentate	Permeate	% Rej	Retentate	Permeate	% Rej	Retentate	Permeate	% Rej
0.0	65,200	53,900	17.3	0.97	0.98	n.a.	0.33	0.25	24.2
48.4	105,700	82,200	22.2	0.72	0.79	n.a.	0.66	0.438	33.6
71.0	150,300	114,800	23.6	0.49	0.63	n.a.	1.05	0.66	37.1
82.3	177,100	147,800	16.5	0.35	0.5	n.a.	1.33	0.94	29.3
Recovery	Potassium (mg/L)			Calcium (mg/L)			Sodium (mg/L)		
(%)	Retentate	Permeate	% Rej	Retentate	Permeate	% Rej	Retentate	Permeate	% Rej
0.0	2,020	922	54.4	335	<5	~100	455	120	73.6
48.4	3,950	1,522	61.5	660	15	97.7	606	207	65.8
71.0	7,040	1,569	77.7	510	<5	~100	1642	224	86.4
82.3	10,850	2,200	79.7	530	<5	~100	1901	309	83.7

Reverse osmosis rejected nearly all the salts and acid. Therefore. RO permeate is suitable for rinsing the columns after regeneration. Nanofiltration rejected potassium in preference to acid. Nanofiltrate contained sufficient acidity (1.2 to 4.6%) to consider its reuse for regeneration. However, it contained significant concentration of potassium (922 to 2,200 mg/L), which reduces its effectiveness.

All retentate samples collected during IXWW concentration trials produced a white precipitate. This precipitate was determined to be calcium sulfate by laboratory analysis. Review of ion exchange literature indicated that calcium has much higher selectivity for cation exchange resins. Discussion with plant management revealed the juice concentration is diluted with well water before ion exchange. Well water contains about 140 mg/L of alkalinity most of which is possibly due to calcium.

Nanofiltration removes all the calcium (>97%), most potassium (~70%) but passes most of the sulfuric acid (~70%). Review of ion exchange theory indicated that dilute acid with significant potassium concentrations can be used effectively to regenerate cation exchange resins. Therefore, nanofiltrate at highest recovery level (80%) was used to regenerate IX resin in the laboratory to evaluate its effectiveness. Table 13 summarizes the results of this exercise.

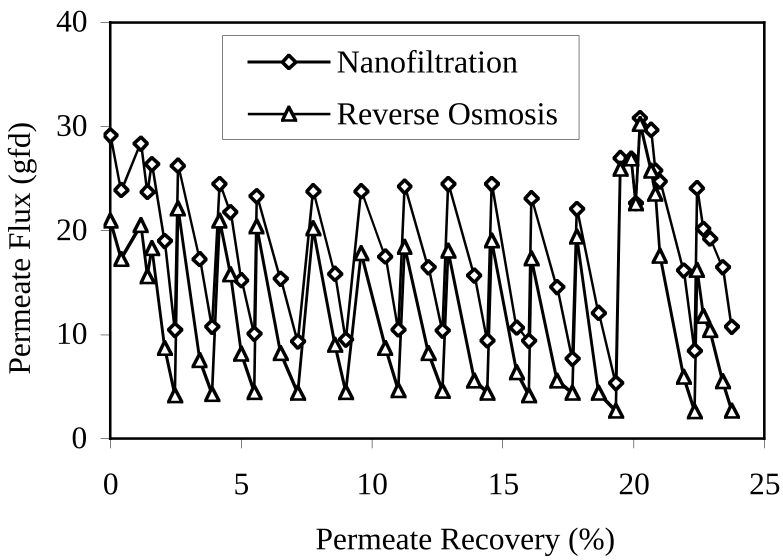
Table 13. Regeneration of IX Resin using IXWW Nanofiltrate and Acid

Regenerant	Acidity (%)	Potassium (mg/L)	Regenerated Resin Capacity (meq/mL)	Regenerated Resin Capacity (% theoretical)
Sulfuric Acid	5.58	0	1.04	54.7
IXWW Nanofiltrate	4.06	2,470	0.79	41.7
IXWW Nanofiltrate + Acid	5.58	2,140	0.92	48.3

The results of this experiment confirmed that IXWW nanofiltrate could be used effectively for regeneration of the resin in spite of its potassium content. When the nanofiltrate was fortified with acid to the standard 5.58% concentration, it was 88% as effective as fresh standard acid.

The flux and separation characteristics obtained in short term trials validated the concept of IXWW treatment. A 24 hour feed and bleed trial was conduced to observe the long-term performance of the membranes. The feed tank was filled with feed heated to 110F. The feed volume was reduced to 50% by draining the RO permeate and to 25% by draining the NF permeate. This procedure was repeated sixteen times over 24 hours. Permeate fluxes observed in this trial are shown in Figure 10.

Figure 10. Flux Characteristics During Treatment of IXWW Pressure 450psi – Temperature 110F



Permeate fluxes decreased rapidly with increase in concentration of the retentate. However, the fluxes increased immediately when fresh feed was introduced. Long term flux decline was small compared to the concentration effect. Nanofiltration membrane produced higher permeate flux than the reverse osmosis membrane again indicating the concentration effect. Membranes cleaned adequately after the trials with a dilute caustic solution.

The trial results confirm that reverse osmosis can be used to reduce the IXWW volume by about 50%. The possibility of using nanofiltration to reduce the volume further while recovering some acid for reuse is indicated but needs further experimental verification.

A preliminary economic assessment of a reverse osmosis system to reduce the 50% of the volume was prepared based on a set of broad assumptions. A single pass standard seawater reverse osmosis system with 6,000 sft of membrane area meets this requirement. This system has to operate on a batch mode. The cost of this system on a skid with a CIP system and the first set of membranes is estimated at $130,000. It is driven by a single 100 hp pump. In a batch operation the pump operates at much lower rating at the beginning and increases pressure and power consumption as concentration increases. Average power consumption of 60 kw was assumed in the absence of more accurate information. An economic assessment based on these assumptions is presented in Table 14.

Table 14. Economic Assessment of Reverse Osmosis System for IXWW

System Parameters	
Reverse Osmosis capacity (gpd)	*50,000*
Capital investment ($)	*130,000*
Electric power (kW)	*75*
Hours of operation (hours/day)	*24*
Days of operation (days/year)	*150*
Permeate production (Mgal/year)	*10*
Expenses ($/year)	
Energy cost (216MWh@$80)	*17,280*
Membrane cost (1 year life)	*18,000*
Cleaning (lump sum)	*2,000*
Total operating costs	***37,280***

The operating cost of the membrane system amounts to $3.73/kgal of permeate. This is much less than the cost of transport. The return of investment for this membrane system is very favorable. The costs of infrastructural needs like buildings, tanks, utilities, etc., should be included in the economic assessment to improve its accuracy.

10.0 Miscellaneous Topics

10.1 Electrodialysis of Wine and Juice

Electrodialysis is an alternative method of wine stabilization that is finding wide acceptance in Europe. Electrodialysis allows for savings in the additives (filtration, seeding) required by the conventional refrigeration processes. Only waste produced by the process is in Membrane cleaning and about 15 gallons of water used in the brine loop per 100 gallons of wine.

The typical investment for a (relatively large) production of 10 million gallons per year system would be in the range of $400,000. Typical operating cost is about 1 cents per bottle. The energy consumption is about 3 kWh per kgal of wine that is substantially less than cold stabilization. A demonstration of electrodialysis is planned in collaboration with Ameridia during Summer 2001.

10.2 Splitting of Potassium Bitartrate

The plant uses potassium hydroxide (KOH) for cleaning evaporators and stills and tartaric acid (TA) in wine making. It is possible to use byproduct potassium bitartrate (KHT) to produce KOH and HT by salt splitting or bipolar electrodialysis. This process has many advantages over the conventional process used to produce HT. The conventional process produces two waste by products, potassium carbonate and calcium sulfate in stoichiometric quantities. Salt splitting process produces two useful products. Only waste in this process is small quantities of membrane cleaning chemicals. Many recently developed organic acid manufacturing processes use bipolar electrodialysis. A research and development effort in this direction is recommended.

10.3 Byproducts of distillation

Byproducts of distillation, aldehydes and fusel alcohols, are some times mixed with still bottoms and disposed by land application. The byproduct output is estimated to be about 400 gallons per hour. At an assumed heating value of 12,000 Btu/lb, the byproduct output has a heating value of 920 million Btu per day. This has a value of $4,600 estimated at $5 per MBtu. Yearly output of byproducts have a fuel replacement value approaching a million dollars.

The possibility of using these byproducts for their heating value should be investigated. One possibility is to use as fuel in the boilers. Dehydrated fuel ethanol has a market value of about $1.40. Industrial ethanol plants mix aldehydes and fusel alcohols with ethanol and market as fuels alcohol. However, dehydrated fusel oils and aldehydes do not seem to have a market by themselves.

The stills at the winery idle most of the year. Industrial alcohol production during the idle time using waste sugar sources in the plant could produce additional revenue and help market fusel oil and aldehydes.

10.4 Sugar Recovery from Grape Pomace

The pomace from grape crushing process is supposed to contain significant amount of sugar. It is possible to extract most of this sugar as a dilute solution by leaching. It can be concentrated by reverse osmosis and fermented to produce food grade or fuel grade ethanol. This process could be tested during the crushing season.

Conclusion

Membrane technology demonstration at Fresno Winery of E. & J. Gallo Winery was successful in identifying several membrane applications with significant benefits. Installation of full scale membrane systems to implement two of these applications began even before the completion of this work. Several other membrane applications and other separation processes will be further evaluated during the upcoming crushing season.